RESEARCH ARTICLE

Preparation and characterization of *p*-sulfonated calix [4] arene functionalized chitosan hydrogel beads and their preliminary adsorption study towards removal of lead (II) and zinc (II) ions

Hamizah Syahirah Mohamad Zubir [a], Mohd Haniff Wahid [a,b,*], Irene Ling[c], Hong Ngee Lim [a,b], Sazlinda Kamaruzaman [a], Zulkarnain Zainal[a]

[a] *Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[b] *Materials Synthesis and Characterization Laboratory (MSCL), Institute of Advanced Technology (ITMA), Universiti Putra Malaysia 43400 UPM Serdang, Selangor, Malaysia*
[c] *School of Science, Monash University Malaysia, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor, Malaysia*

* *Corresponding author: mw_haniff@upm.edu.my*

Abstract

p-sulfonated calix[4]arene functionalized chitosan hydrogel beads have been successfully prepared by mixing *p*-sulfonated calix[4]arene and chitosan in dilute acetic acid solution (1% v/v), followed by dropping the mixture into sodium hydroxide solution to form beads with diameters of ~0.1 cm. The presence of the active sulfonate groups and the unique structure of calixarene render the material useful as an adsorbent for heavy metal ions. Metal adsorption on *p*-sulfonated calix[4]arene is possible through a combination of physical and ionic interactions. Atomic Absorption Spectroscopy (AAS) results showed that the amount of adsorbed metal ion is optimum at 10 ppm for all samples. The overall percentage of metal ion removal shows that *p*-sulfonated calix[4]arene modified chitosan is the best adsorbent with up to 98% removal achieved for Pb(II) and 90% removal for Zn(II). This is followed by *p*-sulfonated calix[4]arene and graphene oxide (GO) modified chitosan with up to 90% removal for Pb(II) and 89% removal for Zn(II) and pure chitosan hydrogel beads with up to 60% removal for both Pb(II) and Zn(II). The results clearly prove that the presence of *p*-sulfonated calix[4]arene can enhance the adsorption of heavy metal ions. In addition, the adsorbent shows higher Pb(II) removal compared to Zn(II).

Keywords: calixarene, chitosan, graphene oxide, hydrogel beads, heavy metal ion removal

INTRODUCTION

There is a major global concern on water quality. The rapid development in industrial and agricultural activities has contributed to the increase in wastes being released to the environment, thus deteriorating water quality. To overcome this problem, various techniques have been introduced to remove different types of pollutants such as heavy metal ions, dyes, nitrates and phosphates, and other hazardous and toxic chemicals from water (Reddy & Lee 2013; Akpor *et al.* 2014; Authman *et al.* 2015; Konczyk *et al.* 2016; Awad *et al.* 2017; Marbu & Benton 2018). Heavy metal ions are commonly found in industrial water effluents which tend to accumulate in both soil and water, posing threats to the living ecosystems as they can be easily transported and taken up (Akpour *et al.* 2014; Authman *et al.* 2015; Konczyk *et al.* 2016). The accumulation of these ions can damage or reduce the function of central nervous system or even cause kidney and liver damages (Akpour *et al.* 2014).

Several methods have been developed to remove heavy metal ions such as chemical coagulation, ion exchange, chemical oxidation/reduction, adsorption, bioremediation, reverse osmosis, membrane separation, electrochemical techniques, and ultrafiltration (Reddy & Lee 2013; Awad *et al.* 2017; Marbu & Benton 2018). Adsorption possesses several advantages over other methods such as simple, cost effective, high efficiency, easy recovery, reasonably high regeneration capacity, and it is sludge-free (Zhang *et al.* 2016). The underlying mechanism for adsorption is based on the favorable interaction between the target metal ion and active groups exist on the surface of adsorbent (Handayani *et al.* 2011). This can be achieved by utilizing chelating ligands or cavitands that has effective binding affinity toward the target metal ions (Konczyk *et al.* 2016; Zawierucha *et al.* 2016; Awad *et al.* 2017). To date, numerous materials have been studied in terms of effectiveness for metal adsorption. One of these materials is calixarene (Siswanta *et al.* 2016) which has a fairly unique molecular geometry with almost unlimited derivate possibilities (Siswanta *et al.* 2016). Calixarenes are present in three-dimensional structures where phenolic sub-units are bridged with methylene and forms a ring with an upper rim, central annulus, and lower rim (Figure 1) with several functional sites (McMahon *et al.* 2003). This enables the modification of their upper or lower rim in order to gain access to derivatives with functional groups selective to the targeted guest ions (Izatt et al. 1985; McMahon et al. 2003). Thus far, calixarenes have been utilized for extraction of various analytes, heavy metal, dyes, and oxyanions (Alahmadi *et al.* 2013).
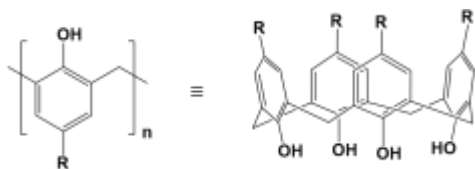
Figure 1 Chemical structure of calix[4]arene and its cup-shaped representation

EXPERIMENTAL

Materials

p-sulfonated calix[4]arene was provided by Dr. Irene Ling from Monash University. Zinc chloride (extra pure) and lead powder (≥99% trace metal basis) were obtained from HmbG Chemicals and Sigma Aldrich, respectively. Sodium hydroxide and glacial acetic acid were obtained from Merck. High molecular weight chitosan was obtained from Friendmann Schmidt Chemical. Graphene oxide solution was provided by Dr Lim Hong Ngee from UPM which was synthesized using the modified Hummers' method (Lim *et al.* 2011). All materials were used as received without any further purification.

Preparation of chitosan hydrogel beads

A schematic diagram representing the preparation of the calixarene functionalized chitosan hydrogel beads is as shown in Figure 2. In a typical preparation of chitosan hydrogel beads, 0.2 g of high molecular weight chitosan was dissolved in 12.5 µL of acetic acid and 20 mL deionized (DI) water. The chitosan solution was added drop-wise into 50% w/v sodium hydroxide solution. The formed chitosan hydrogel beads were collected and washed with DI water.

Preparation of *p*-sulfonated calix[4]arene / chitosan (C4SCTS) hydrogel beads and *p*-sulfonated calix[4]arene / chitosan / graphene oxide (C4SCTSGO) hydrogel beads.

Firstly, 0.1 g of *p*-sulfonated calix[4]arene was dissolved in DI water and diluted in 100 mL volumetric flask. Next, chitosan solution was prepared by dissolving 0.2 g of chitosan in 12.5 µL of acetic acid and 10 mL DI water. To prepare *p*-sulfonated calix[4]arene / chitosan (C4SCTS) solution, 10 mL of *p*-sulfonated calix[4]arene stock solution was added into chitosan solution.

Meanwhile for the preparation of *p*-sulfonated calix[4]arene / chitosan containing graphene oxide, 1 mL of GO (1 mg / mL in water solution) was added into 10 mL of *p*-sulfonated calix[4]arene solution and then added into the chitosan solution. Calixarene modified mixture was then added drop-wise in 50% w/v sodium hydroxide solution using 5 mL syringe and let aside for the beads to form. The hydrogel beads that were formed were filtered and washed with DI water.
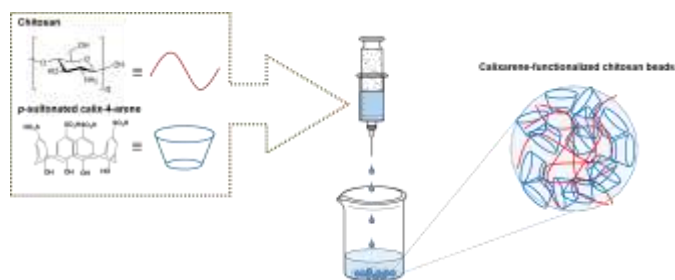

Figure 2 Schematic diagram for preparation of *p*-sulfonated calix[4]arene functionalized chitosan hydrogel beads. Chitosan are represented as red colored linear chains while calixarenes are represented as blue cup-shaped structures attached on the side chains.

Preparation of heavy metal ion solution

This work involved two metal ions solutions which were Zn(II) and Pb(II) metal ion solutions. To prepare these solutions, 1.0 g of zinc chloride was dissolved in 30 mL of 5 M HCl and diluted with deionized water in 1000 mL volumetric flask, whereas 1.0 g of lead powder was dissolved in 30 mL 5 M nitric acid, and diluted with DI water in 1000 mL volumetric flask. Different concentrations of Zn(II) and Pb(II)

metal ion solutions were prepared from the stock solutions, namely 1 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm.

Heavy metal ion adsorption test

To study the ability of the samples to adsorb heavy metal ions, the adsorption test was carried out using different concentrations of heavy metal ion solution, namely; 20 ppm, 15 ppm, 10 ppm, 5 ppm, and 1 ppm. 5 pieces of the hydrogel beads were added into 10 mL of heavy metal ion solution and stirred at 5 rpm for 30 minutes. Percent removal of heavy metal ions was calculated using the following equation:

$$\text{Percent removal} = \frac{(C_i - C_f)}{C_i} \times 100\% \qquad \text{Eq. 1}$$

where C_i is the initial concentration of metal ion solution and C_f is the final concentration of metal ion solution. The filtrate solutions obtained in the adsorption process were analyzed using Atomic Absorption Spectrometer (AAS) where the initial and final concentration of heavy metal ion solution was investigated.

RESULTS AND DISCUSSION

Preparation of hydrogel beads

Hydrogel beads of pristine chitosan (CTS), *p*-sulfonated calix[4]arene functionalized chitosan (C4SCTS), and *p*-sulfonated calix[4]arene functionalized chitosan with addition of graphene oxide were successfully prepared. As shown in Figure 3 (a) and (b), both CTS and C4SCTS hydrogel beads are spherical (0.1 cm diameter) and white in color. Meanwhile, C4SCTSGO hydrogel beads appeared light brown
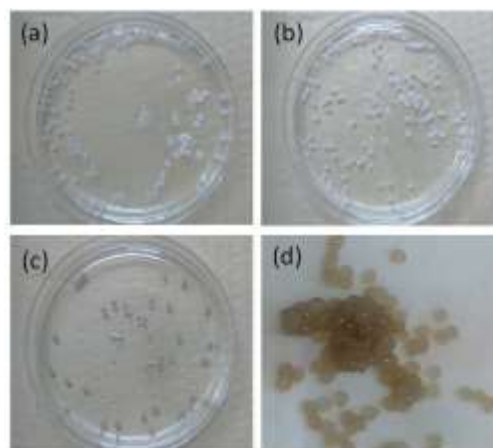

Figure 3 Hydrogel beads of (a) pure chitosan (CTS), (b) *p*-sulfonatocalix[4]arene/chitosan (C4SCTS), (c) *p*-sulfonatocalix[4]arene/chitosan/graphene oxide (C4SCTSGO) and (d) enlarged image of (c)

IR spectra of CTS, C4SCTS, and C4SCTSGO hydrogel beads were recorded and are shown in Figure 4. The IR spectrum for CTS displays the typical absorption bands of chitosan as reported in the literatures (Fig. 4) (Yuwei & Jianlong 2011; Queiroz *et al.* 2015). A strong absorption band at 3300 cm^{-1} – 3400 cm^{-1} is attributed to N-H and O-H stretching, along with the intramolecular hydrogen bonds (Yuwei & Jianlong 2011; Queiroz *et al.* 2015). Meanwhile, the absorption peaks at around 2890 and 2860 cm^{-1} can be attributed to C-H symmetric and asymmetric stretching, respectively (Queiroz *et al.* 2015). A band at 1589 cm^{-1} corresponding to the N-H bending of the primary amine was also discernible (Queiroz *et al.* 2015). The CH$_2$ bending and CH$_3$ symmetrical deformation vibrations were vindicated with the presence of bands at around 1423 and 1375 cm^{-1}, respectively. The absorption band at 1153 cm^{-1} can be attributed to asymmetric stretching vibration of the C-O-C bond. The bands at 1066 and 1028 cm^{-1} correspond to C-O stretching (Queiroz *et al.* 2015). It is noteworthy to point out that for the spectrum of C4SCTS hydrogel beads, most of the absorption peaks are attributed to functional groups present in chitosan since chitosan is dominant in the composite. Therefore, functional groups of calixarene molecule either overlap with the absorption peak of chitosan's

functional groups or appear as small absorption peaks due to low concentration (Panchal *et al.* 2010). For instance, peaks attributed to vibrational mode of sulfonate groups (vSO_3) was reported to appear at ~1050 cm^{-1} – ~1200 cm^{-1} which overlaps with the C-O stretching absorption peaks (Panchal *et al.* 2010). For the same reason, IR spectrum for C4SCTSGO also displays similar absorption peaks as CTS since it is dominant in the sample and in addition, the functional groups exist in GO are also similar as CTS (Ciplak *et al.*, 2014).
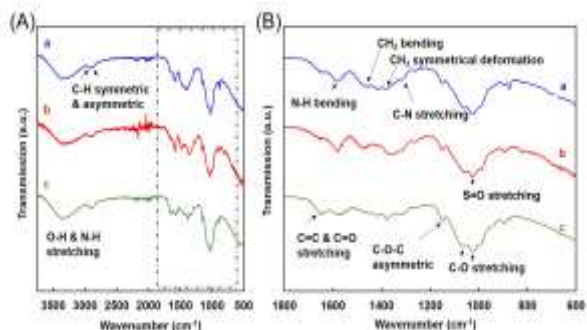

Figure 4 FTIR spectra of (A) Prepared hydrogel beads and (B) Expanded spectra from the inset in A. Lowercase a, b and c represents spectra of CTS, C4SCTS and C4SCTSGO hydrogel beads respectively.

Adsorption study of Pb(II) and Zn(II) using Atomic Absorption Spectroscopy (AAS)

The adsorbent's heavy metal ions removal ability was tested by measuring the concentration of heavy metal ions left in the solution using a Thermo Scientific SOLAAR M series AAS. The adsorption behavior of Pb(II) and Zn(II) by the adsorbents at various initial concentrations (1 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm) are as summarized in Figure 5a and b. All operational parameters were kept constant (agitation speed: 100 rpm, pH: 5, contact time: 30 minutes). Based on the results obtained, increasing the initial concentrations of metal ions causes an increase in the adsorption capacity with the highest removal rate attained at 10 ppm. However, at higher than 10 ppm initial heavy metal ion concentration, the adsorption shows decreasing trend with increase of Pb(II) and Zn(II) ions concentration. This could be due to at low ion concentration, the ratio of the surface active sites to the total metal ions in the solution is high. Hence, all metal ions may interact with the adsorbent and efficiently be removed from the solution. However, at concentrations higher than 10 ppm, the adsorbent presumably has reached the saturation limit causing limited active sites for metal binding. Therefore, more metal ions were remaining in solution at higher concentration levels.

The highest percentage of Pb(II) ion removal was recorded at 98.83%, 90.65% and 60.58% by C4SCTS, C4SCTSGO and CTS hydrogel beads respectively (Fig. 4a). Meanwhile, for the removal of Zn(II) ion, (Fig. 4b) the highest was recorded at 90.93%, 89.62% and 60.42% by C4SCTS, C4SCTSGO and CTS hydrogel beads respectively. For both cases, the removal of Pb(II) and Zn(II) ions are the highest at 10 ppm and decrease as the initial concentration increased. Result shows that C4SCTS hydrogel beads display the best adsorption performance followed by C4SCTSGO hydrogel beads and CTS. This strongly suggests that the presence of active functional groups of calixarene, such as sulfonate and hydroxyl groups play important role in the removal of the heavy metal ions. Interestingly, adsorbent containing GO shows lower adsorption performance, possibly due to the GO layers covering the functional groups of the calixarene molecules thus decreasing the number of available metal binding sites. Nevertheless, hydrogel beads containing GO are physically more robust compared to samples without GO. Results also show that the sorption efficiency for all adsorbents is higher for Pb(II) compared to Zn(II) metal ions.
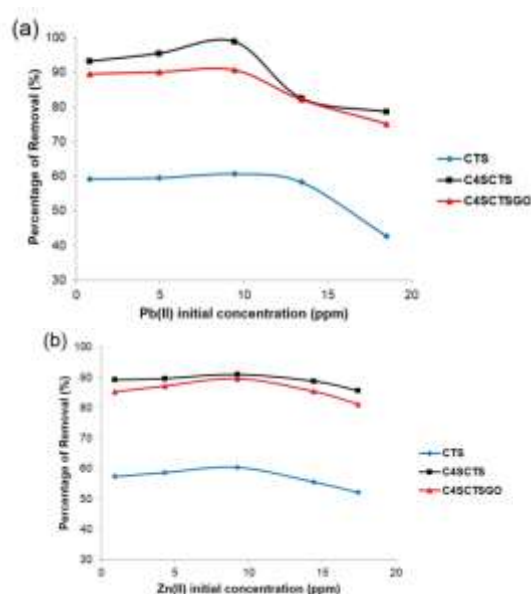

Figure 5 Percentage of (a) Pb(II) and (b) Zn(II) metal ion removal by different adsorbents at different concentrations

Morphological study using Scanning Electron Microscopy (SEM)

The morphology of CTS, C4SCTS, and C4SCTS hydrogel beads after introduced into 10 ppm Pb(II) metal ion solution were studied by Scanning Electron Microscope (SEM). SEM images of CTS and C4SCTS hydrogel beads are shown in Figure 6.
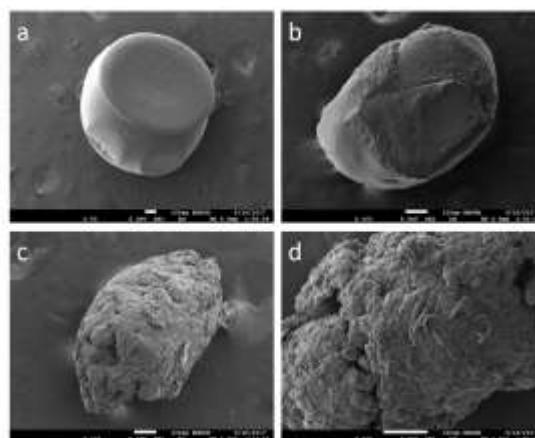

Figure 6 SEM images of (a) CTS hydrogel beads, (b) C4SCTS hydrogel beads, (c) C4SCTS hydrogel beads after introduced into metal ion solution (Pb(II), 10 ppm) and (d) enlarged image of (c).

As shown in Figure 6a, pure chitosan hydrogel beads obtained are spherical in shape with smooth surface. However, in the presence of *p*-sulfonated calix[4]arene, the surface of the hydrogel beads became slightly rough and less spherical. Interestingly, after adsorbing heavy metal ions, the surface of the hydrogel beads shows significant changes where the surface became rough, possibly due to result of binding interactions with heavy metal ions (Fig. 6c and d).

CONCLUSION

An efficient adsorbent based on calixarene modified chitosan were successfully prepared using a facile technique. Results show that maximum removal of Pb(II) and Zn(II) by C4SCTS hydrogel beads was achieved at 10 ppm initial heavy metal ion concentration with 98.83% and 90.93% removal, respectively. This indicates that upon addition of *p*-sulfonated calix[4]arene into chitosan, the metal ion adsorption capacity of the hydrogel beads has dramatically increased. Meanwhile, the addition of graphene oxide did not contribute towards metal ion removal, however the stability of the hydrogel towards shrinkage was

slightly improved in which the hydrogels without GO shrinks easier compared to the hydrogels with GO if left in open atmosphere for a prolonged period of time.

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REFERENCES

Akpour, O. B., Ohiobor, G. O., Olaolu, T. D. 2014. Heavy metal pollutants in wastewater effluents: Sources, effects and remediation. *Advances in Bioscience and Bioengineering*, 2014, 2(4): 37-43.

Alahmadi, S. M., Mohamad, S., Maah, M. J. 2013. Preparation of organic-inorganic hybrid materials based on MCM-41 and its applications. *Advances in Materials Science and Engineering,* 2013, Article ID 634863.

Ashwin, B. C. M. A., Saravanan, C., Senthilkumaran, M., Sumathi, R., Suresh P., Mareeswaran, P. M. 2018. Spectral and electrochemical investigation of p-sulfonatcalix[4]arene stabilized vitamin E aggregation. *Supramolecular Chemistry,* 30(1): 32-41.

Authman, M. M. N., Zaki, M. S., Khallaf, E. A., Abbas, H. H. 2015. Use of fish as bio-indicator of the effects of heavy metals pollution. *Journal of Aquaculture Research and Development,* 6(4): 1000328.

Awad, F. S., AbouZeid, K. M., Abou El-Maaty, W. M., El-Wakil, A. M., El-Shall, M. S. 2017. Efficient removal of heavy metals from polluted water with high selectivity for mercury (II) by 2-imino-4-thiobiuret–partially reduced graphene oxide (IT-PRGO). *ACS Applied Materials & Interfaces,* 9:34230−342420

Ciplak, Z., Yildiz, N., Calimli, A. 2014. Investigation of graphene-Ag nanocomposites synthesis parameters for two different synthesis methods. *Fullerenes Nanotubes and Carbon Nanostructures,* 23(4): 361-370.

Handayani, D. S., Siswanta, D., Ohto, K., Kawakita, H. 2011. Adsorption of Pb (II), Cd (II), and Cr (III) from Aqueous Solution by Poly-5-allyl-calix [4] arene tetra carboxylic acid. *Indonesian Journal of Chemistry* 1,1(2): 191–195.

Izatt, R. M., Bradshaw, J. S., Nielsen, S. A., Lamb, J. D., Christensen, J. 1985. Thermodynamic and kinetic data for cation-macrocycle interaction. *Chemical Reviews,* 85(4): 271-339.

Konczyk, J., Zajac, A. N., Kozlowski, C. 2016. Calixarene-based extractants for Heavy Metal Ions Removal from Aqueous Solutions. *Separation Science and Technology,* 51(14): 2394-2410.

Lim. H. N., Huang, N. M., Lim, S. S., Harrison, I., Chia, C. H. 2011. Fabrication and characterization of graphene hydrogel via hydrothermal approach as a scaffold for preliminary study of cell growth. *International Journal of Nanomedicine,* 6: 1817–18230

Marpu, S. B., Benton, E. N. 2018. Shining light on chitosan: A Review on the usage of chitosan for photonics and nanomaterials research. *International Journal of Molecular Sciences,* 19: 1795.

McMahon, G., O'Malley, S., Nolan, K., Diamond, D. 2003. Important Calixarene Derivatives: Their Synthesis and Applications. *Arkivoc* (vii): 23-31.

Panchal, J. G., Patel, R. V., Menon, S. K. 2010. Preparation and physicochemical characterization of carbamazepine (CBMZ): para-sulfonated calix[n]arene inclusion complexes. *Journal of Inclusion Phenomena and Macrocyclic Chemistry,* 67: 201–2080

Prabawati, S. Y., Jumina, Santosa, S. J., Mustofa, Ohto, K. 2012. Study on the adsorption properties of novel calix[6]arene polymers for heavy metal cations. *Indonesian Journal of Chemistry,* 12(1): 28–34.

Queiroz, M. F., Melo, K. R. T., Sabry, D. A., Sassaki, G. L., Rocha, A. O. 2015. Does the use of chitosan contribute to oxalate kidney stone formation? *Marine Drugs,* 13: 141-158.

Reddy, D. H. K., Lee, S. M. 2013. Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. *Advances in Colloid and Interface Science,* 201–202: 68–93.

Siswanta, D., Jumina, J., Anggraini, M., Mardjan, M. I. D., Mulyono, P., Ohto, K. 2016. Adsorption study of Pb(II) on Calix[4]resorcinarene Chitosan Hybrid. *International Journal of Applied Chemistry,* 12(1): 11–22.

Yuwei, C., Jianlong, W. 2011. Yuwei (2011) preparation and characterization of magnetic chitosan nanoparticles and its application for Cu(II) removal. *Chemical Engineering Journal,* 168: 286-292.

Zawierucha, I., Kozlowski, C., Malina, G. 2016. Immobilized materials for removal of toxic metal ions from surface/groundwaters and aqueous waste streams. *Environ. Sci.: Processes Impacts* 18: 429-444.

Zhang, L., Zeng, Y., Cheng, Z. 2016. Removal of heavy metal ions using chitosan and modified chitosan: A review. *Journal of Molecular Liquids,* 214: 175–191.